Residual Solvents by Headspace Analysis

1.0 Scope and Application

1.1 This method was adapted from the United States Environmental Protection Agency's "SW-846 Test Method 5021A: Volatile Organic Compounds (VOCs) in Various Sample Matrices Using Equilibrium Headspace Analysis."

1.2 This method describes equilibrium-based static headspace preparation of volatile organic compounds (VOCs) in cannabis concentrates by gas chromatography (GC) or gas chromatography/mass spectrometry (GC/MS). This method is applicable to a wide range of organic compounds that have sufficiently high volatility to be effectively removed from samples using the described conditions. While the method is designed for use on samples containing low levels of VOCs or dilutions thereof to be analyzed by direct vapor partitioning, a solvent extraction and extract introduction procedure is also described for solid samples containing high concentrations of VOCs or for oily materials that may not be appropriate for the low-level technique. This preparation method is intended to be combined with a determinative method. This preparation method is appropriate for the compounds listed below, and it may also be appropriate for other VOCs included in the determinative method, provided method performance is demonstrated to be acceptable for the intended use of the data.

Solvent	µg/g	ppm (simplified)	CAS No.
Acetone	5.0 * 103	5000	67-64-1
Benzene	2	2	71-43-2
Butanes (Sum of Isomers)	5.0 * 103	5000	
• n-butane			106-97-8
• 2-methylpropane (isobutane)			75-28-5
Cyclohexane	3.9 * 103	3880	110-82-7
Chloroform	2	2	67-66-3
Dichloromethane	6.0 * 102	600	75-09-2
Ethanol	5.0 * 103	5000	64-17-5
Ethyl acetate	5.0 * 103	5000	141-78-6
Heptanes (Single Isomer)	5.0 * 103	5000	
• n-heptane			142-82-5
Hexanes (Sum of Isomers)	2.9 * 102	290	
• n-hexane			110-54-3
• 2-methylpentane			107-83-5
• 3-methylpentane			96-14-0
• 2,2-dimethylbutane			75-83-2
• 2,3-dimethylbutane			79-29-8
Isopropanol (2-propanol)	5.0 * 103	5000	67-63-0
Methanol	3.0 * 103	3000	67-56-1
Pentanes (Sum of Isomers)	5.0 * 103	5000	
• n-pentane			109-66-0

• methylbutane (isopentane)			78-78-4
• dimethylpropane (neopentane)			463-82-1
Propane	5.0 * 103	5000	74-98-6
Toluene	8.9 * 102	890	108-88-3
Xylenes (Sum of Isomers)	2.2 * 103	2170	
• 1,2-dimethylbenzene (ortho-)			95-47-6
• 1,3-dimethylbenzene (meta-)			108-38-3
• 1,4-dimethylbenzene (para-)			106-42-3

1.3 The following compounds may also be analyzed by this procedure or may be used as surrogates:

Compound	CAS No.
Bromobenzene	108-86-1
n-Butylbenzene	104-51-8
sec-Butylbenzene	135-98-8
tert-Butylbenzene	98-06-6
2-Chlorotoluene	95-49-8
4-Chlorotoluene	106-43-4
cis-1,2-Dichloroethene	156-59-4
1,3-Dichloropropane	142-28-9
2,2-Dichloropropane	590-20-7
1,1-Dichloropropene	563-58-6
Isopropylbenzene	98-82-8
4-Isopropyltoluene	99-87-6
n-Propylbenzene	103-65-1
1,2,3-Trichlorobenzene	87-61-6
α,α,α-Trifluorotoluene	98-08-8
1,2,4-Trimethylbenzene	95-63-6
1,3,5-Trimethylbenzene	108-67-8

1.4 In order to produce quantitative data with this technique, all of the quality control criteria described in the determinative method should be met. Alternatively, this method may be utilized as a screening protocol. If used for screening, semi-quantitative or estimated sample results may be obtained with minimal calibration and quality control, such as a reagent blank and a single calibration standard.

As with any preparative method for volatiles, screening samples prior to low level analysis may help minimize problems associated with carryover contamination from samples that contain very high concentrations of volatiles above the calibration range of the determinative method. In addition, because removing a sample aliquot from a container may compromise the integrity of the sample, multiple sample aliquots should be collected to allow for screening and re-analysis.

1.5 In order to accommodate analysis of a variety of sample matrices and VOCs, a matrix modifier (Sec. 6.6) is generally recommended to be used with this method. The matrix modifier is a water-soluble salt solution that is added to each sample and standard vial prior to analysis. The matrix modifier solution acts to increase the VOCs mass transfer into the headspace of the vial. The principal benefits of using the matrix modifier are:

1. better response and reproducibility of the VOCs that do not otherwise partition efficiently into the headspace of the vial from the aqueous phase; and

2. less potential for measurement bias resulting from aqueous activity differences between standards and samples.

Measurement bias results from VOCs partitioning into the vial headspace differently in a sample than in the calibration standards. Some potential sources of measurement bias and the anticipated effects of the matrix modifier on these sources of bias are described below.

1.6 Measurement of VOCs using this method may be subject to bias from several sources, including differences in partitioning of VOCs between the aqueous phase and headspace in samples relative to standards, differences in headspace volume in samples relative to standards, and adsorption of VOCs to surfaces or absorption into compatible phases. Measurement bias is monitored through internal standard, surrogate, and matrix spike recovery when appropriate for the determinative method. Use of the matrix modifier (Sec. 6.6) will help minimize measurement bias resulting from differences in partitioning behavior of VOCs in samples relative to standards. Measurement bias resulting from adding solid material to the vial, which changes the headspace volume in the sample relative to the calibration standards, is expected to be negligible as long as the volume of material is small relative to the headspace volume. The magnitude of this bias may be reduced by adding a similar volume of solid organic-free control material to calibration standards as the volume of the bulk material being tested. Measurement bias related to sorption of VOCs to solid samples with fine particle size distributions and/or significant organic content may be substantial. The magnitude of this bias may be reduced by analyzing a smaller amount of material or by solvent extraction (Sec. 10.4).

1.7 Prior to employing this method, analysts are advised to consult the base method for each type of procedure that may be employed in the overall analysis for additional information on quality control procedures, development of QC acceptance criteria, calculations, and general guidance. Analysts also should consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

1.8 This method is restricted to use by, or under supervision of, appropriately experienced and trained analysts for volatile organic analysis in general and specifically the use of equilibrium headspace devices interfaced to the determinative method selected by the analyst. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 Summary of the Method

2.1 Sample collection and vial preparation.

Surrogates and internal standards may be added to the vials during sampling or at the laboratory. If the matrix modifying solution is used for the analysis and was not added to sample vials at the time of collection, it should be added when any surrogates and internal standards are added at the laboratory. Adding the matrix modifying solution or reagent water to a vial after adding the sample may cause loss of gas phase VOCs from the container due to displacement of a portion of the vial headspace. Adding the matrix modifying solution (Sec. 6.6) to the vial prior to adding the sample and sealing quickly will help to limit loss of VOCs from the sample container and maintain sample representativeness.

NOTE: The choice of chemical preservative(s) will depend on the VOCs that will be measured in the samples and to some extent on the sample matrix. The matrix modifying solution acts as a chemical preservative, but it does not otherwise alter the sample pH and may not protect against degradation of some classes of VOCs.

2.1.1 High concentration solid materials — A representative portion of sample is collected with an appropriately sized tool and placed in a glass VOA vial, and then the vial is sealed. The sample may be preserved by addition of extraction solvent at the time of sampling or upon receipt by the laboratory.

NOTE: Surrogate compounds may either be spiked into the solvent at the time of extraction or into reagent water containing an aliquot of the extract prior to analysis. Since the surrogate recovery data from these two options provides assurances of either extraction or analytical efficiencies, the decision as to when the surrogates are added depends on what questions need to be answered for a given sample matrix and the intended uses of the data.

2.2 In the laboratory, the vials are rotated to allow for diffusion of internal standards and surrogates throughout the matrix. The vials are placed in the autosampler carousel of the headspace analyzer and maintained at room temperature. Approximately 1 hour prior to analysis, the individual vials are moved to a heated zone and mechanically agitated while the elevated temperature is maintained, allowing the VOCs to equilibrate between the headspace, liquid and any solid phases in the vial.

2.3 The autosampler then pressurizes the vial with helium and forces a portion of the headspace gas mixture into the gas chromatograph through a heated transfer line, either passing through the GC inlet or directly connected to the analytical column via an inert, low dead volume connector.

2.4 Determinative analysis is performed using the appropriate GC or GC/MS method. Any chemical preservative and matrix modifier added to customer samples should also be added to the calibration standards and other QC samples.

3.0 Interferences

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation may be necessary. Refer to each method to be used for specific guidance on quality control procedures and to Chapter Four for general guidance on the cleaning of glassware. Also refer to the determinative methods to be used for information regarding potential interferences.

3.2 Volatile organic analyses are subject to major interference problems because of the prevalence of volatile organics in a laboratory.

3.3 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride) through the septum seal of the sample vial during shipment and storage. A trip blank, prepared from an appropriate organic-free matrix and sample container and carried through sampling and handling protocols, serves as a check on such contamination.

3.4 The sample matrix itself can cause severe interferences by one of several processes or a combination of these processes. These include, but are not necessarily limited to, oily material which inhibit the partitioning of the volatile target analytes into the headspace. Therefore, analyte recovery by direct vapor partitioning may be low and will depend on the properties of the particular chemical. This matrix effect can be difficult, if not impossible, to overcome. It is recommended that surrogates or additional deuterated compounds (for GC/MS methods) be added to a matrix and analyzed to determine the percent recovery of these compounds. The calculated percent recovery can give some indication of the degree of the matrix effect, but not necessarily correct for it. Alternatively, the use of the high-concentration procedure in this method should minimize the problem with oily waste.

3.5 Contamination by carryover can occur whenever high concentration and low concentration samples are analyzed sequentially. Where practical, samples with unusually high concentrations of analytes should be followed by an analysis of one or more method blanks or instrument blanks to check for cross-contamination. If the target compounds present in an unusually concentrated sample are also found to be present in subsequent samples, the analyst must demonstrate that the compounds are not affected by carryover contamination. Conversely, if those target compounds are not present in the subsequent sample, then the analysis of a blank is not necessary.

3.6 The laboratory where volatiles analysis is performed should be free of any solvents that may interfere with the analysis. Special precautions must be taken when analyzing for methylene chloride. The analytical and sample storage areas should be isolated from all atmospheric sources of methylene chloride. Otherwise, random background levels can result. Since methylene chloride can permeate through polytetrafluoroethylene (PTFE) tubing, all GC carrier gas lines and purge gas plumbing should be constructed of stainless steel or copper tubing. Laboratory workers' clothing previously exposed to methylene chloride fumes during common liquid/liquid extraction procedures can contribute to sample contamination. The presence of other organic solvents in the laboratory where volatile organics are analyzed can also lead to random background levels, and the same precautions must be taken.

3.7 Ethers in acidic samples (i.e., samples with a pH < 7) will hydrolyze at the higher temperatures used in this method. As such, basic preservatives should be used if the target analytes are ethers or the alcohols that those ethers would form if hydrolyzed. Strong bases may catalyze substitution and elimination reactions that can occur if halogenated compounds are present. Halogenated aliphatic VOCs are particularly susceptible to dehydrohalogenation reactions in neutral to basic conditions at elevated temperature such as with a heated sample preparation procedure as is described here. Accordingly, acidic preservatives may be necessary to prevent dehydrohalogenation if halogenated aliphatic

VOCs are analytes of interest or their presence is suspected and their transformation products are of interest. Acetone has also been observed to form in high organic content preserved with sodium bisulfate. The chemical reactivity introduced by the preservative should be monitored by analyzing a matrix spike of a customer sample with each batch. The spiking solution should contain all analytes which the client intends to monitor.

4.0 Safety

This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals included in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

5.0 Equipment and Supplies

The mention of trade names or commercial products in this manual is for illustrative purposes only and does not constitute a WSDA endorsement or exclusive recommendation for use. The products and instrument settings cited in these methods represent those products and settings used during method development or subsequently evaluation. Glassware, reagents, supplies, equipment, and settings other than those listed in this manual may be employed provided that method performance appropriate for the intended application has been demonstrated and documented.

This section does not list all common laboratory glassware (e.g., beakers and flasks) that might be used.

5.1 Headspace containers: Clear glass, 22-mL vials equipped with PTFE-lined septa that are compatible with the analytical system. Vials of other sizes may be employed, provided that they can be hermetically sealed and equipped with suitable septa. Ideally, the vials and septa should have a uniform tare weight. The septa should be unpunctured, as piercing the PTFE face may allow target analytes to diffuse into and adsorb to the silicone backing material. New, disposable vials may be used without pretreatment provided they are demonstrated to be clean through method blank analysis. Store the vials in an area free of organic solvents. If vials are suspected of being a source of contamination, first wash the vials in a detergent solution, then thoroughly rinse with tap water followed by distilled water, and finally dry the vials in an oven at 105° C for 1 hour. Allow vials to cool prior to use.

5.2 Headspace system: The operating conditions listed in Sec. 10.0 are those selected for the equipment used in developing this method. Other equipment and conditions may be employed, provided that the laboratory demonstrates performance for the analytes of interest using the determinative method appropriate for the intended application. The system used must meet the following specifications:

5.2.1 The system must be capable of holding samples at elevated temperatures and establishing a reproducible equilibrium between a wide variety of sample types and the headspace.

5.2.2 The system must be capable of accurately transferring a representative portion of the headspace into a gas chromatograph fitted with a capillary column without adversely affecting the chromatography or the detector.

5.3 Miscellaneous equipment

5.3.1 For the preparation of blanks, standards, and water samples, it is necessary to have the crimping tool available in the laboratory.

5.3.2 Graduated microsyringes for standard preparation and for addition of internal standard and surrogate spiking solutions.

5.3.3 5mL glass hypodermic syringes with Luer-Lok™ tip (other sizes are acceptable depending on sample volume used).

6.0 Reagents and Standards

6.1 Reagent-grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Reagents should be stored in glass to prevent the leaching of contaminants from plastic containers.

6.2 Extraction solvent: Pesticide quality or equivalent. Store away from other solvents. Purchase in small quantities (1 Liter size or less) to minimize shelf life to reduce potential for contamination.

6.3 See the determinative method for guidance on the preparation of stock standards and a secondary standard for internal standards, calibration standards, and surrogates.

6.3.1 Calibration spiking solutions: Prepare five or more spiking solutions in water that contain all the target analytes. The concentrations of the calibration solutions should be such that the addition of 1.0 µL of each to the headspace vials will bracket the analytical range of the detector. Alternatively, calibration standards may be prepared by adding different volumes of one or more stock solutions provided that the linearity of the calibration is not affected by the methanol content. For analysis of methanol extracts, it may be appropriate to calibrate surrogates at multiple concentration levels as well to demonstrate calibration linearity at the surrogate level measured in diluted extracts.

6.3.2 Internal and surrogate standards: Follow the recommendations of the determinative method for the selection of internal and surrogate standards. Selection and use of surrogates with physical properties similar to the classes of target analytes that are of interest for the project will provide more meaningful sample-specific quality assurance information. A concentration of 20 mg/L for both internal and surrogate standards may be used for spiking each sample. The concentration may vary depending on the relative sensitivity of the detector used in the determinative method. If determination is by GC, external standard calibration may be preferred, and the internal standard omitted.

6.4 Blank preparation: Transfer 10.0 mL of matrix modifying solution (Sec. 6.6) or 0.2 grams matrix blank to a sample vial. Inject the necessary amounts of internal standards and surrogate in the headspace vial and seal the vial. Place in the autosampler and analyze in the same manner as an unknown sample. Any chemical preservative and/or matrix modifier added to the customer samples must also be included in the blank(s).

6.5 Preparation of calibration standards: Prepare calibration standards in the same manner as blanks, adding the standard spiking solution(s) in the same manner that internal standards and surrogates are added. Any chemical preservative and/or matrix modifier added to the customer samples should also be included in the calibration standards.

6.6 Preparation of matrix-modifying solution: Add 180 g of ACS-grade sodium chloride (NaCl) to 500 mL of reagent water. Mix well until all components are dissolved. Other water-soluble salts may be appropriate. The matrix modifier solution should not affect the pH of the sample to the extent that preservation or analyte stability is compromised. Analyze a 10.0-mL portion from each batch to verify that the solution is free of contaminants. Store the prepared matrix-modifying solution in a sealed bottle in an area free of organic chemicals at ≤6 °C.

6.7 Preparation of chemical preservative for low level (vapor partitioning) analysis - The preservative should be chosen based on the analytes of interest and should be mixed with the sample at the time of sampling.

6.7.1 If a basic preservative is chosen, 100 mg of ACS-grade trisodium phosphate dodecahydrate (TSP; Na3PO4•12H2O) should be added to a 22-mL headspace vial.

7.0 Sample Collection, Preservation, and Storage

Sample collection, preservation and storage requirements may vary by program and may be specified in a rule or regulation that requires compliance monitoring for a given contaminant. Where such requirements are specified in the regulation, follow those requirements. In the absence of specific regulatory requirements, use the following information as guidance in determining an appropriate plan for sample collection, preservation and storage prior to sample collection and analysis.

7.1 All samples should be stored in capped vials at ≤6 °C in an area free of solvent fumes. If any evidence of leakage is found, the sample can be considered corrupted and should be discarded.

7.2 Sample storage

7.2.1 Samples shall be stored at ≤6 °C until analysis in order to limit evaporative loss of the analytes, reduce the ability of the analytes to react with the glass walls of the sampling container and further hinder sample biodegradation. Cannabis samples in VOA vials with no headspace should not be frozen, but subsamples added to prepared headspace vials may be frozen, provided the integrity of the container seal is maintained. The sample storage area should be free of organic solvent vapors.

7.2.2 All samples shall be analyzed within 14 days of collection or sooner if labile compounds are target analytes.

8.0 Quality Control

8.1 Refer to testing method for guidance on quality assurance (QA) and quality control (QC) protocols. Individual method rules may also contain QC criteria specific only to that method. The QC criteria in the rules take precedence over chapter QC criteria.

Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated. All data sheets and quality control data should be maintained for reference or inspection.

8.2 Initial Demonstration of Proficiency (IDP)

Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat the demonstration of proficiency whenever new staff members are trained or significant changes in instrumentation are made.

8.3 Limit of Quantitation (LOQ) check standard

The laboratory shall establish the LOQ as the lowest point of quantitation, which in most cases, is the lowest concentration in the calibration curve. LOQ verification is recommended for each method to validate quantitation capability at low analyte concentration levels. This verification may be accomplished with either clean control material or a representative sample matrix, free of target compounds. Optimally, the LOQ should be less than the desired regulatory action levels based on the stated data quality objectives.

In order to demonstrate the entire sample preparation and analysis process at the lower limit of quantitation (LOQ), a LOQ check standard (not part of an initial calibration) is prepared by spiking a clean control material with the analyte(s) of interest at the predicted LOQ concentration level(s). Alternatively, a representative sample matrix may be spiked with the analytes of interest at the predicted LOQ concentration levels. The LOQ check is carried through the same preparation procedures as cannabis samples and other QC samples.

Recover of target analytes in the LOQ check standard should be within established specific acceptance limits, to demonstrate acceptable method performance at the LOQ. Until the laboratory has sufficient data to determine acceptance limits, the LCS criteria ± 20% may be used for the LOQ acceptance criteria. This acknowledges the poorer overall response at the low end of the calibration curve. Historically based LOQ acceptance criteria should be determined as soon as practical once sufficient data points have been acquired.

8.4 Initially, before processing any samples, the analyst should demonstrate that all parts of the equipment in contact with the sample and reagents are interference-free. This is accomplished through the analysis of a method blank. As a continuing check, each time samples are extracted, cleaned up, and analyzed, and when there is a change in reagents, a method blank should be prepared and analyzed for the compounds of interest as a safeguard against chronic laboratory contamination. If a peak is observed within the retention time window of any analyte that would interfere with measurement of that analyte, determine the source and eliminate it, if possible, before analyzing the samples. The blanks should be carried through all stages of sample preparation and analysis. When new reagents or chemicals are received, the laboratory should monitor method and/or instrument blanks associated with samples for any signs of contamination.

The laboratory should not subtract the results of the method blank from those of any associated samples. Such "blank subtraction" may lead to negative sample results. If the method blank results do not meet the specific acceptance criteria and reanalysis is not practical, then the data user should be provided with the sample results, the method blank results, and a discussion of the corrective actions undertaken by the laboratory.

8.5 Sample quality control for preparation and analysis

The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, bias, method sensitivity). At a minimum, each batch of 20 or fewer customer samples should include at least one method blank, a laboratory control sample (LCS), and either a matrix spike/matrix spike duplicate (MS/MSD) pair or a matrix spike and duplicate analysis of one cannabis sample. When used, surrogates may be added to each sample and QC sample and their recovery monitored to evaluate the effect of the sample matrix. Any method blanks, matrix spike samples, and duplicate QC samples should be subjected to the same analytical procedures (Sec. 10.0) as those used on actual samples.

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

8.7 The laboratory should have quality control procedures to make sure that sample integrity is not compromised during the sample collection and sample handling process, e.g., method blanks, etc. In addition, it would be advisable for the laboratory to monitor the internal standard (IS) area counts for all samples; leaks attributed to a poor seal with the vial caps and septa will be evident by low IS area counts. Sample containers and data results for instances where low IS area counts are observed and leaks are suspected should be discarded. Low area counts of the less volatile internal standards may also be attributed to matrix effects and should not be confused with a leaking vial.

8.8 Heating the sample/chemical preservative/matrix modifier mixture can exacerbate chemical interferences such as those introduced by acid catalyzed hydrolysis or base catalyzed substitution and elimination reactions. This can only be monitored through a matrix spike of a sample from every analytical batch. The spiking solution should be the same as that used to prepare the calibration standards in order to minimize sources of variability in evaluating spike recovery. The acceptance criteria shall be those recommended in the determinative method or specified by a properly executed systematic planning document. If these criteria cannot be met, the analyst may adjust the pH of the mixture through the addition of solid $NaHSO_4$ to excessively basic mixtures or solid $Na_3PO_4 \cdot 12H_2O$ to excessively acidic mixtures. After this is done, the matrix spike analysis should be repeated with an unanalyzed vial. If the results are acceptable, this pH adjustment should be made to all samples in the appropriate analytical batch. Even if the pH-adjusted matrix spike analysis is acceptable, the data user must be made aware that the initial matrix spike failed and the pH adjustment was necessary. The results from the pH adjusted samples should be reported, and the data user must be made aware that the results for the analytes for which the initial matrix spike failed are questionable.

9.0 Calibration and Standardization

Sec. 10.0 for information on calibration and standardization and refer to the appropriate determinative method for additional calibration and standardization procedures.

10.0 Procedure

10.1 Sample preparation: Sample preparation in the laboratory will be necessary. The procedure for sample preparation depends upon the matrix of the sample and the target analyte concentration range. To minimize loss of VOCs from the samples or exchange of the vial headspace with the room air, add spiking solutions quickly to cold sample vials soon after removing from refrigerated storage and either reseal or place a new cap on top of the vial and apply slight pressure in between preparation steps.

CAUTION: Adding standard solutions (e.g., internal standards) to a sealed vial by puncturing the PTFE septum face with a microsyringe exposes the gas phase contents of the vial to the silicone material backing the septum. This material may absorb some of the gas phase VOCs in the vial, causing problems with calibration, measurement in samples, spike recovery, etc., as a function of exposure time. This problem is generally worse for the higher molecular weight VOCs with high octanol-water partition coefficients, and this practice should be avoided, or the vial caps should be exchanged for caps with un-punctured septa soon after spiking if these VOCs are analytes of interest.

10.1.1 Cannabis samples: If the sample will be analyzed by direct vapor partitioning for low level analysis, follow the instructions in this section. If the sample will be extracted with solvent and the extract diluted for high level analysis, proceed to Sec.10.4.

10.1.1.1 If the sample was placed into a headspace vial without matrix modifier and the sample mass was not recorded at time of collection, estimate the sample mass by weighing the vial plus sample and subtract the mass of an empty vial and cap. Then, unseal the vial, add 10.0 mL of matrix modifying solution, if used, or extraction solvent, along with any internal standard and/or surrogate standard used, and immediately reseal the vial. VOC losses may occur as a result of opening the vial and displacing 10 mL of headspace.

CAUTION: Only open and prepare one vial at a time to minimize loss of volatile organics.

10.2 The low-concentration method utilizing an equilibrium headspace technique is found in Sec. 10.3 and sample preparation for the high-concentration method is found in Sec. 10.4. The high-concentration method is recommended for samples that obviously contain oily material or organic material.

10.3 Low- concentration (direct vapor partitioning) method for cannabis samples amenable to the equilibrium headspace method.

10.3.1 Calibration: Prior to using this introduction technique for any GC or GC/MS method, the system must be calibrated. Normally, external standard calibration is preferred for the GC methods because of possible interference problems with internal standards. If interferences are not a problem, based on historical data, internal standard calibration is acceptable. The GC/MS methods normally utilize internal standard calibration. The GC/MS methods require instrument tuning prior to proceeding with calibration.

10.3.1.1 If a GC/MS determinative method is employed, prepare a headspace vial containing extraction solvent and the amount of 4-bromofluorobenzene (BFB) listed in the determinative method. If the manufacturer has a recommended tuning agent other than BFB it is also acceptable to use it.

10.3.1.2 Prepare a minimum of five headspace vials for calibration standards and a reagent blank and proceed according to Sec.10.3.2 and the determinative method selected. The mixing step is unnecessary because no sample is present in the vial.

10.3.1.3 Calibration verification: Prepare a headspace vial by spiking with the mid-concentration calibration standard. Proceed according to Sec. 10.3.2.1 (beginning by placing the vial into the autosampler) and the determinative method. If a GC/MS determinative method is employed, prepare a second headspace vial containing extraction solvent and the amount of BFB listed in the determinative method.

10.3.2 Headspace: The conditions described throughout Sec. 10.3 were experimentally optimized using the equipment described in Reference #1 in Sec. 16 and employing Method 8260 as the determinative method. If other headspace systems and determinative methods are utilized, it is recommended that the manufacturer's headspace operating conditions be followed, provided that they are appropriate for the determinative method to be employed.

10.3.2.1 Mix the samples (on a rotator or shaker) for at least 2 min. For samples that contain water insoluble materials, care must be exercised during mixing to prevent this material from adhering to the inner surface of the vial seal; otherwise, the sampling needle can become contaminated with this material upon puncturing the seal. Care must also be exercised to avoid over filling the vial to prevent contaminating the needle with aqueous sample.

Place the vials in the autosampler carrousel at room temperature. The individual vials are heated to 85 °C and allowed to equilibrate for 50 min. Each sample is mixed by mechanical agitation during this equilibrium period. Each vial is pressurized with helium carrier gas to a minimum pressure of 10 psi.

10.3.2.2 A representative and reproducible sample of the pressurized headspace is transferred to the GC column through a heated transfer line according to the manufacturer's instructions.

10.3.2.3 Proceed with the analysis as per the determinative method of choice.

NOTE: If maintaining a specified pH is critical to quality assured measurement of the analyte(s) of concern (Sec. 3.7), the pH of each sample should be verified. If basic preservation is necessary, the pH of the sample should be verified to be ≥10. If acid preservation is necessary, the pH should be verified to be ≤ 2. This check may be performed after analysis of the sample in order to avoid compromising sample integrity. Wide-range pH paper should provide sufficient information to verify efficacy of the preservative.

10.4 High-concentration method

10.4.1 If the sample was collected without the addition of extraction solvent to the vial, then weigh the sample to the nearest 0.01 g. Add twice the volume of extraction solvent as the nominal sample mass to a tared VOA vial and immediately reseal the vial. Open only one vial at a time to minimize loss of VOCs. If the sample was collected in a sealable container, add the extraction solvent to a vial first, weigh the vial with the solvent and the cap together to obtain the tare mass, and then add the sample, seal immediately, reweigh, and calculate the sample mass.

10.4.2 If the sample was collected and either the matrix modifying solution or extraction solvent was added to the sample vials, subsamples for high concentration analysis should be taken from the separate VOA vials collected without matrix modifying solution or extraction solvent. Transfer approximately 0.25 g of sample from the 40 or 60 mL VOA vial into a tared VOA vial containing 10.0 mL of extraction solvent, seal the vial, and reweigh to estimate the mass of sample transferred. Open only one vial at a time to minimize the loss of volatile organics. Substantial VOC losses may occur as a result of transferring a subsample from one vial to another using this procedure.

10.4.3 Mix by shaking for 10 min at room temperature. Decant 2 mL of the solvent extract to a screw-top vial with PTFE-faced septa and seal. Withdraw 10 µL and inject into a headspace vial containing 10.0 mL of matrix modifying solution or extraction solvent. A larger volume of solvent may be added provided the solvent content does not adversely affect the analyte responses. Add internal standards and/or surrogates as appropriate and analyze by the headspace procedure by placing the vial into the autosampler and proceeding with Sec. 10.3.2.1.

11.0 Data Analysis and Calculations

There are no data analysis and calculation steps directly associated with this procedure. Follow the directions given in the determinative method.

12.0 Pollution Prevention

12.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

12.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical Management for Waste Reduction*, a free publication available from the American Chemical Society (ACS), Committee on Chemical Safety.

13.0 Waste Management

13.1 The WSDA requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The WSDA urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions.

14.0 References

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14.4 USEPA OUST, Environmental Fact Sheet: Analytical Methods for Fuel Oxygenates, EPA 510-F-03-001, April 2003.

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14.6 RCRA Organic Methods Workgroup Meeting Minutes, March 20, 2012.

14.7 RCRA Organic Methods Workgroup Meeting Minutes, March 22, 2012.

14.8 RCRA Organic Methods Workgroup Meeting presentation describing changes to Method 5021, “Proposed Changes to SW-846 Method 5021A, VOCs by Static Headspace,” March 1, 2012.

15.0 Acknowledgements

The above method was adapted from the United States Environmental Protection Agency’s “SW-846 Test Method 5021A: Volatile Organic Compounds (VOCs) in Various Sample Matrices Using Equilibrium Headspace Analysis” by the Cannabis Laboratory Analysis Standards Program to meet the recommendations of the Cannabis Science Task Force as a standard method for determining residual solvents for certified cannabis laboratories in the state of Washington.